

The addition of iron to Ni_3S_2 electrode for sodium secondary battery

Jong-Seon Kim^a, Gyu-Bong Cho^a, Ki-Won Kim^a, Jou-Hyeon Ahn^b, Guoxiu Wang^{a,c}, Hyo-Jun Ahn^{a,*}

^aSchool of Materials Science and Engineering, i-Cube Center, ReCAPT, WCUNGB, Gyeongsang National University, 900 Gazwadong, Jinju, Gyeongnam 660-701, Republic of Korea

^bDepartment of Chemical & Biological Engineering, Gyeongsang National University, 900 Gazwadong, Jinju, Gyeongnam 660-701, Republic of Korea

^cDepartment of Chemistry and Forensic Science, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia

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ABSTRACT

In order to investigate the role of iron additive in the Ni_3S_2 electrode, the Ni_3S_2 electrode was prepared by addition of iron. The discharge properties of $\text{Na}/\text{Ni}_3\text{S}_2$ cells using 1 M NaCF_3SO_3 in tetra(ethylene glycol) dimethyl ether liquid electrolyte were investigated at room temperature. The $\text{Na}/\text{Ni}_3\text{S}_2$ cell had an initial discharge capacity of 400 mAh g^{-1} with a plateau potential at 0.84 V versus Na/Na^+ . The discharge capacity decreased to 255 mAh g^{-1} after 15 cycles. Iron additive in Ni_3S_2 electrode played a role as a conductive agent and did not form iron sulfide during charging.

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1. Introduction

The large scale batteries for electric vehicles (EVs), hybrid electric vehicles (HEV) and electricity storage system need a high energy density, safety, long cycle life and low cost [1]. Especially, the material cost is very important for large scale batteries. From this viewpoint, the sodium battery is a better candidate than the lithium battery because sodium is cheap due to its abundance. Sodium/sulfur battery was developed at the Ford corporation in 1968 and operated at high temperature above 300°C . The sodium/sulfur battery showed high theoretical specific energy density of 760 Wh/kg , low cost and long cycle life [2]. However, both sodium and sulfur were in the liquid state at this operation temperature, which might induce a leakage of liquid materials, an explosion, or corrosion in Na/S battery [3]. Some researchers have studied sodium batteries operating at room temperature, because the sodium and sulfur were in solid state at room temperature, which was safer than a liquid state. However room temperature Na/S batteries had a short cycle life [4–6]. Sodium/metal-sulfide cells as well as sodium/sulfur cells showed good electrochemical properties at room temperature [7–10]. Especially, the $\text{Na}/\text{Ni}_3\text{S}_2$ cell showed a high capacity and good cycle life [9]. The Ni_3S_2 electrode consisted of a Ni_3S_2 active material, a PEO binder and Super-P conductive agent. Iron is one of transition metal with a high electric

conductivity and also iron sulfides are good active materials for sodium battery [7,8]. When iron powder was added to the Ni_3S_2 electrode, the role of iron in electrochemical reaction was not reported.

In this study, the Ni_3S_2 electrode containing Fe additive was prepared. The effect of iron addition was investigated from charge and discharge curves, surface morphology and crystal structure of $\text{Na}/\text{Ni}_3\text{S}_2$ cells.

2. Experimental

Nickel sulfide (Ni_3S_2) powders were bought from Aldrich Chemical Co. The diameter of Ni_3S_2 powders decreased below $10 \mu\text{m}$ by ball-milling for 2 h. Carbon black (Super-P, MMM Carbon) dried in an oven at 80°C , iron powder ($<10 \mu\text{m}$, Alfa) and poly (ethylene oxide) (PEO, molecular weight 4×10^6 , Aldrich) were used without pretreatment. Two kinds of nickel sulfide electrodes were prepared. One was Ni_3S_2 electrode containing iron additive and would be represented as $\text{Ni}_3\text{S}_2(\text{Fe})$. The $\text{Ni}_3\text{S}_2(\text{Fe})$ slurry was prepared by mixing Ni_3S_2 powder (60 wt.%), PEO (20wt.%), Super-P (20 wt.%) by addition of iron powder corresponding to one fourth of Ni_3S_2 powder weight (15%) and acetonitrile (Aldrich). The slurry was mixed homogeneously by a planetary ball-mill for 3 h. The homogeneous slurry was pasted on an Al foil substrate by a doctor blade method and then the slurry was dried at 60°C for one day. The dried cathode film was cut into a disc shape of 1.0 cm diameter. In order to compare with $\text{Ni}_3\text{S}_2(\text{Fe})$ electrode, the Ni_3S_2 electrode of same composition without iron powder was made. Sodium anode

* Corresponding author. Tel.: +82 55 751 5308; fax: +82 55 759 1745.

E-mail address: ahj@gnu.ac.kr (H.-J. Ahn).

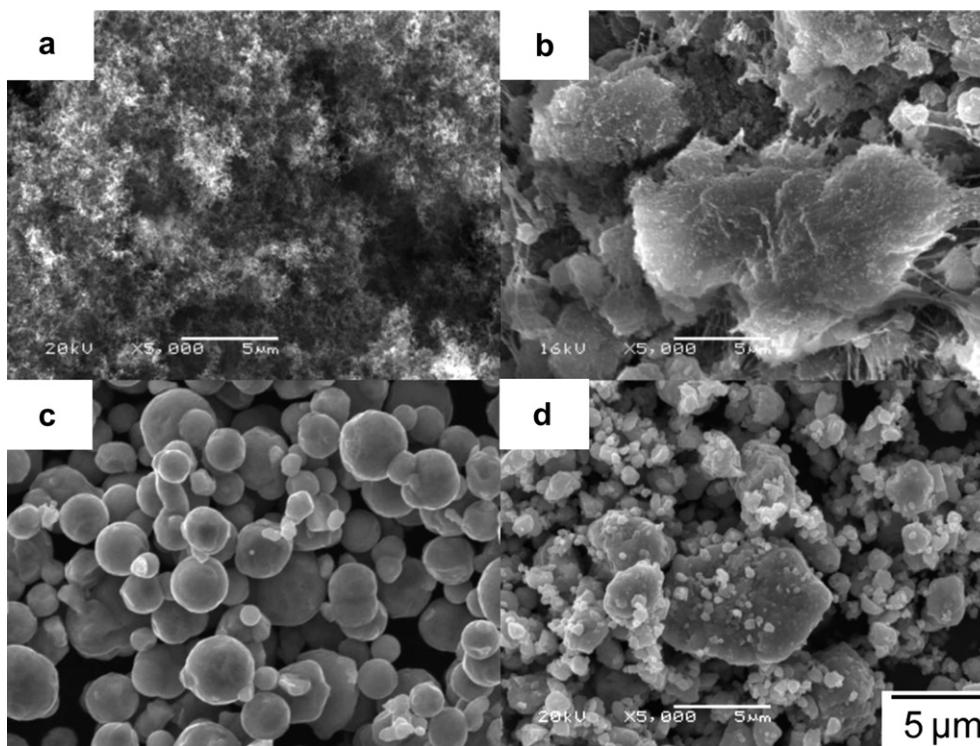


Fig. 1. SEM images of raw powders with (a) Super-P, (b) PEO, (c) Fe and (d) Ni_3S_2 prepared for Ni_3S_2 electrode containing Fe additive.

was prepared by cutting sodium bulk (Aldrich). A liquid electrolyte was prepared by 1 M sodium trifluoromethanesulfonate (NaCF_3SO_3 , Aldrich) salt in tetra(ethylene glycol)dimethyl ether (TEGDME, Aldrich). The cells were assembled by sandwiching the separator including a liquid electrolyte between a sodium anode and the $\text{Ni}_3\text{S}_2(\text{Fe})$ electrode in Ar-filled glove box.

The electrochemical tests were performed using WBCS 3000 battery tester (WonA Tech) at room temperature. The $\text{Na}/\text{Ni}_3\text{S}_2$ and $\text{Na}/\text{Ni}_3\text{S}_2(\text{Fe})$ cells were discharged and charged galvanostatically at voltage range from 0.4 V to 2.6 V and current density was 450 mA g^{-1} (1C-rate). In order to confirm products during the charge–discharge reaction, X-ray diffraction (D8 Discover with GADDS, Bruker) patterns were obtained using $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (JEOL JSM 5600) was employed to observe the surface morphology. Elemental mapping of the electrode was measured using an energy dispersive spectrometer

(INCA Energy, Oxford Instruments). AC impedance measurement was performed with amplitude of 10 mV under a frequency range of 10^6 – 10^{-2} Hz (VMP3, Bio Logic).

3. Results and discussion

Fig. 1 shows SEM morphologies of raw materials for the Ni_3S_2 electrode which are Super-P, PEO, Ni_3S_2 and Fe powders. Carbon black had a particle size below $1 \mu\text{m}$ with very large surface areas. PEO particles were agglomerated. Iron powder had spherical shape below $5 \mu\text{m}$ in size.

The X-ray diffraction patterns of the raw materials are presented in **Fig. 2**. Carbon showed two broad peaks, which could be related to a nanocrystalline or amorphous structure. The sharp peak of PEO indicated a crystalline structure. XRD peaks of iron powder showed

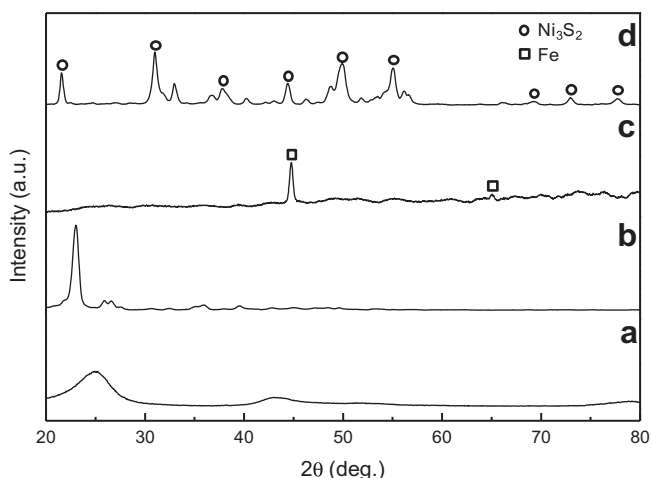


Fig. 2. XRD patterns of raw powders with (a) Super-P, (b) PEO, (c) Fe and (d) Ni_3S_2 .

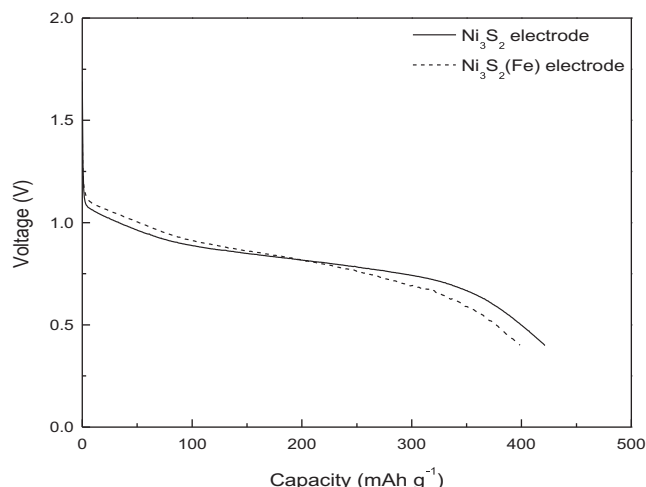


Fig. 3. Discharge curves of $\text{Na}/\text{Ni}_3\text{S}_2$ cell and $\text{Na}/\text{Ni}_3\text{S}_2(\text{Fe})$ cell at 1 C.

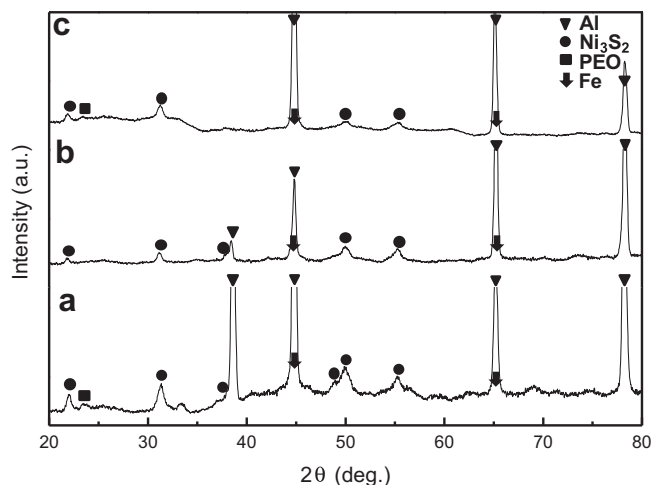


Fig. 4. X-ray diffraction data of Na/Ni₃S₂ cells containing Fe additive at (a) original electrode, (b) 1st discharged electrode and (c) 1st charged electrode.

44.7° and 65.0° corresponding to the cubic structure (JCPDS # 87-0721). The majority of the XRD peaks of the Ni₃S₂ powder were coincided with the rhombohedral structure (JCPDS # 85-1802), which was the stable structure of Ni₃S₂ at room temperature.

Fig. 3 shows the first discharge curves of Na/Ni₃S₂ and Na/Ni₃S₂(Fe) cells with a current density of 450 mA g⁻¹ at room temperature. The first discharge curve of the Na/Ni₃S₂ cell had a potential plateau at 0.84 V and a discharge capacity of 420 mAh g⁻¹, which were similar as the previous report [9]. The Na/Ni₃S₂(Fe) cell also showed a similar discharge curve with the Na/Ni₃S₂ cell.

Fig. 4 shows the change in XRD profiles of the Ni₃S₂(Fe) electrode during the electrochemical discharge–charge reaction. The original electrode showed X-ray peaks of Ni₃S₂, Al and PEO phases. Aluminum peaks came from an aluminum current collector. Iron peaks could not be identified due to overlapping with large aluminum peaks at 44.6 and 65°. XRD pattern of discharged electrode showed the same phase as the original electrode. However, the peak intensity of Ni₃S₂ phase decreased. After charge reaction, the intensity of Ni₃S₂ peaks did not change. During charging and discharging process, the peak intensity of Ni₃S₂ phase decreased

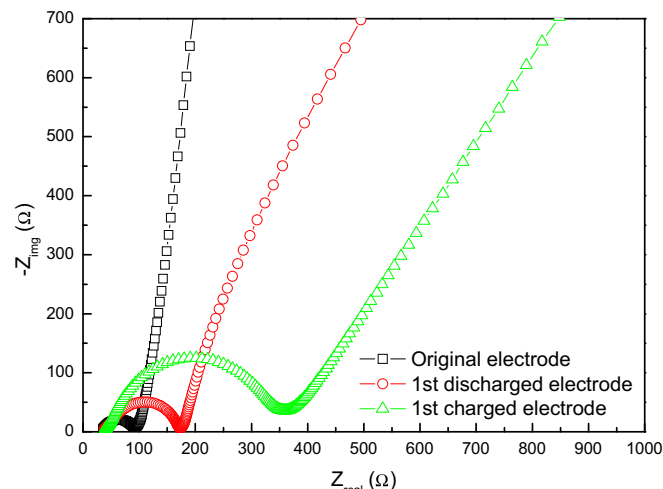
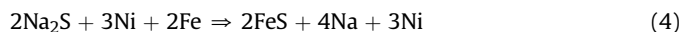
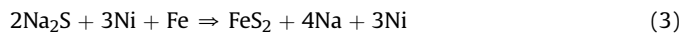
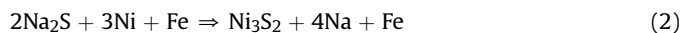


Fig. 6. AC impedance data of a Na/Ni₃S₂ cell containing Fe additive.

but no new peaks were detected. We reported charge and discharge reaction (1) of Na/Ni₃S₂ cell in previous work [9]. A charge and discharge process of the Na/Ni₃S₂ cell was explained as follows.



During charging process, Na₂S and Ni could form Ni₃S₂ active material. When iron powder is put into the Ni₃S₂ electrode, the charge process of Na/Ni₃S₂(Fe) cell could be explained as the following equations.



If eq. (2) took place, iron could play as a conductive agent. If eq. (3) or (4) was possible, iron could form active material of iron sulfides such as FeS and FeS₂. After charging, iron sulfide peaks of FeS and FeS₂ phases did not appear in Ni₃S₂(Fe) electrode. Also, we could not find the plateau potential of 1.2 V in Fig. 3 which was

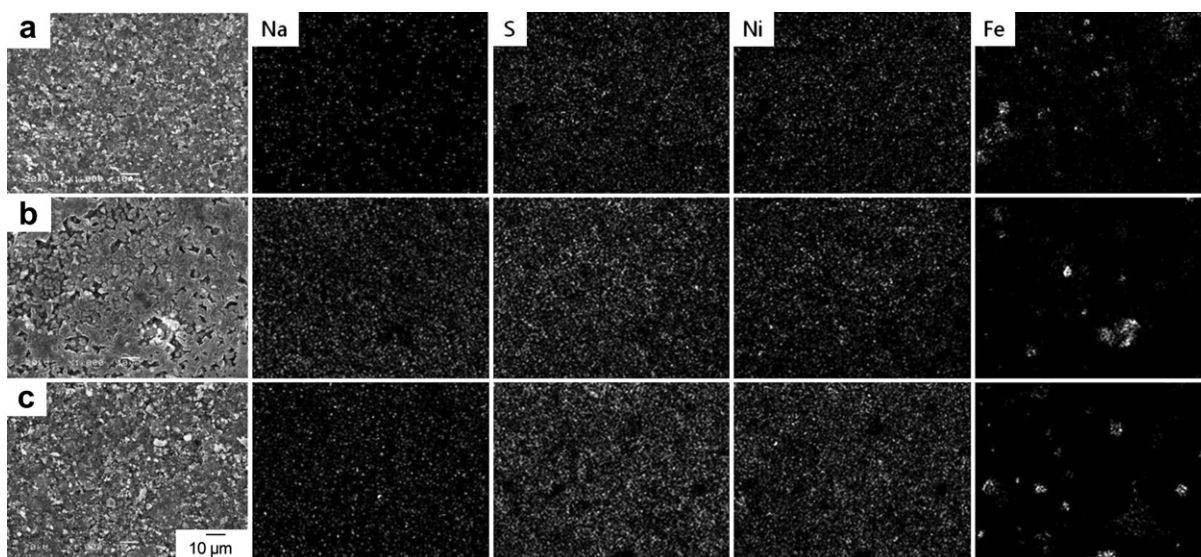


Fig. 5. SEM images and elemental mapping data of (a) original electrode, (b) 1st discharged electrode and (c) 1st charged electrode.

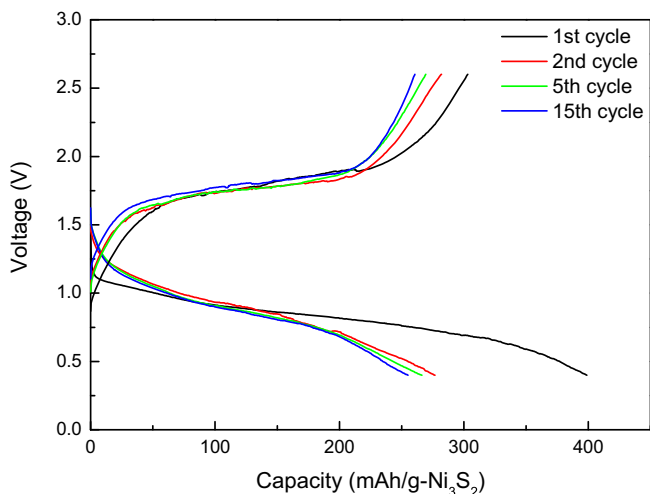


Fig. 7. Galvanostatic charge and discharge curves of a Na/Ni₃S₂ cell containing Fe additive.

observed in Na/FeS₂ cell [2]. From the results of Figs. 3 and 4, and eq. (2), iron sulfides were not formed during charging process, and the role of iron should be conductive agent not active materials. Since XRD peaks of Ni, Na₂S, or NaNi₃S₂ phase could not be observed, the Ni and Na₂S phases might be composed of smaller nanograins than the X-ray coherence length [11].

Fig. 5 shows the changes of SEM images and elemental mapping data for the Ni₃S₂(Fe) electrode during charging and discharging. Original electrode showed homogeneous distribution of nickel and sulfur caused by Ni₃S₂ powder. After the first discharge, the electrode surface was covered by a dense film that was different from the surface of an original Ni₃S₂ electrode. This phenomenon was similar to the previous works of Na/Ni₃S₂ and Na/Cu₂S cells and this film might be related to discharged products [9,10]. However, the surface of charged electrode was similar as the original shape. In addition, sodium was not detected in iron mapping area, which could explain the role of iron as a conducting agent. After charging, the bright regions were composed of sulfur, nickel, iron and sodium components, which might come from Ni₃S₂, Na₂S, Fe and Ni phases. From the discharge curve, XRD and EDS data, iron powder in the

Ni₃S₂ electrode played the role as only a conductive agent instead of active material.

Fig. 6 shows AC impedance spectra of the Na/Ni₃S₂(Fe) cells. The impedance spectrum was composed of one semicircle and a short straight sloping line. These parts could be respectively assigned to the spectra of the bulk resistance and interfacial resistance. The bulk resistances of Na/Ni₃S₂(Fe) cell did not change by discharging or charging. However, the interfacial resistance of Na/Ni₃S₂(Fe) cell increased drastically after discharge and charge reaction. Initial resistance was determined by the properties of the passivation layers formed on the surface of electrodes in contact with the electrolytes. The change of interfacial resistance might be related with the surface changes shown in Fig. 5 during cycling.

Fig. 7 shows the changes of charge and discharge curves of the Na/Ni₃S₂(Fe) cell during repeated cyclings. The first charge curve showed a plateau potential of 1.8 V and high irreversible capacity of 100 mAh g⁻¹. After second cycles, the discharge curve showed slopping phenomena and reversible behavior was observed during charging and discharging. Fig. 8 shows the cycle performance of Na/Ni₃S₂(Fe) cell. After the second cycle, coulombic efficiency of the Na/Ni₃S₂(Fe) cell was very high. The discharge capacity was maintained about 255 mAh g⁻¹, which was smaller than the Na/Ni₃S₂ cell [9]. These results could be explained by two possible reasons. One was the high current density of 450 mA g⁻¹ which is higher than that of the previous one (50 mA g⁻¹). Another reason might be related with iron conducting agents which was less effective than super-P.

4. Conclusions

Ni₃S₂ electrode was prepared by addition of iron powder. The charge–discharge characteristics of the Na/Ni₃S₂(Fe) have been investigated at room temperature. The Na/Ni₃S₂ cell gave an initial discharge capacity of 400 mAh g⁻¹ with a plateau potential region at 0.84 V versus Na/Na⁺ at room temperature and also showed good cycle performance over 15 cycles. Iron powder in the Ni₃S₂ electrode played a role as a conductive agent and does not form iron sulfides.

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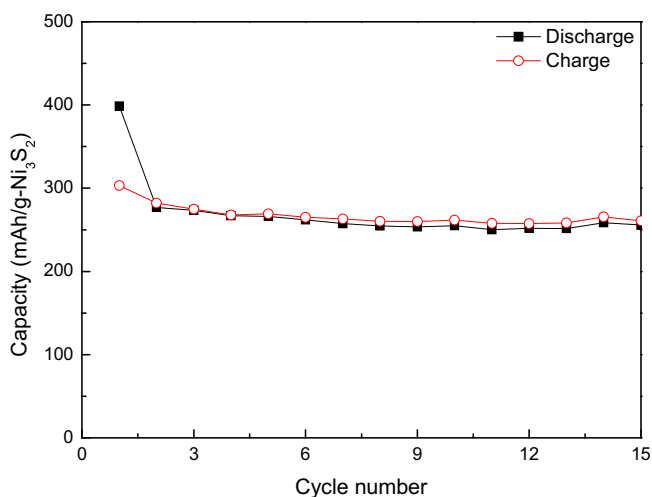


Fig. 8. Charge and discharge capacity as a function of cycle number of a Na/Ni₃S₂ cell containing Fe additive.